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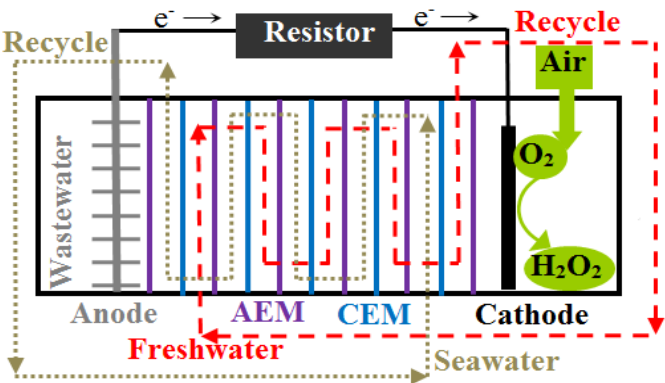
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Highlights

- Microbial reverse-electrodialysis electrolysis cell for H₂O₂ production.
- High yield synthesis of H₂O₂ from oxygen reduction without external power supply.
- Salinity-gradient between salt and fresh water drove the high-rate H₂O₂ production
- Recycling the salt and fresh water for the production with less water consumption.
- Cathode potential as key for H₂O₂ production can be adjusted by air flow rate.

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Salinity-Gradient Energy Driven Microbial Electrosynthesis of Hydrogen Peroxide

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Abstract

Hydrogen peroxide (H_2O_2) as a strong oxidant, is widely used in various chemical industries and environmental remediation processes. In this study, we developed an innovative method for cost-effective production of H_2O_2 by using a microbial reverse-electrodialysis electrolysis cell (MREC). In the MREC, electrical potential generated by the exoelectrogens and the salinity-gradient between salt and fresh water were utilized to drive the high-rate H_2O_2 production. Operational parameters such as air flow rate, pH, cathodic potential, flow rate of salt and fresh water were investigated. The optimal H_2O_2 production was observed at salt and fresh water flow rate of 0.5 mL min^{-1} , air flow rate of $12\text{-}20 \text{ mL min}^{-1}$, cathode potential of $-0.485 \pm 0.025 \text{ V}$ (vs Ag/AgCl). The maximum H_2O_2 accumulated concentration of $778 \pm 11 \text{ mg L}^{-1}$ was obtained at corresponding production rate of $11.5 \pm 0.5 \text{ mg L}^{-1} \text{ h}^{-1}$. The overall energy input for the synthesis process was $0.45 \pm 0.03 \text{ kWh kg}^{-1} \text{ H}_2\text{O}_2$. Cathode potential was the key factor for H_2O_2 production, which was mainly affected by the air flow rate. This work for the first time proved the potential of MREC as an efficient platform technology for simultaneous electrosynthesis of valuable chemicals and utilization of salinity-gradient energy.

Keywords: Microbial electrosynthesis; H_2O_2 ; Microbial reverse-electrodialysis electrolysis cell; Salinity gradient; Cathode potential; Wastewater

1. Introduction

H_2O_2 is an environmentally friendly oxidant for various industries and environmental treatment processes, such as pulp and paper bleaching, textile applications, detergent applications, municipal wastewater treatment. It is manufactured industrially mainly through the anthraquinone oxidation [1], which is an energy-intensive and unsustainable process. Thus, sustainable and cost-effective methods for H_2O_2 production are being pursued [2, 3].

In recent years, microbial electrochemical technologies have gained increasing attention for energy generation, water treatment, bioremediation and chemical synthesis. Among METs, microbial fuel cell (MFC) [4, 5] and microbial electrolysis cell (MEC) [6-9] have been demonstrated as alternative approach to produce H_2O_2 through two electrons reduction of O_2 . The H_2O_2 concentration in MFCs was only ranging from 79 to 196 mg L^{-1} [4, 5]. Comparatively, the maximum H_2O_2 concentration close to 1.3 g L^{-1} was produced in MEC at an applied voltage of 0.5 V [6]. By using MFC as external power supply, a relatively high H_2O_2 concentration of 439 mg L^{-1} was also achieved in MEC [9]. Thus, in the view of production rate and accumulated concentration, MEC is more efficient over MFC for H_2O_2 production [8]. However, the external power supply (in whatever form) required by MEC may add the costs to the synthesis process, especially for long-term operation, and thereby hindering its practical application.

Recently, a novel type of microbial electrochemical technologies called microbial reverse-electrodialysis cell (MRC) or microbial reverse-electrodialysis electrolysis cell (MREC), which combines a reverse electrodialysis cell (RED) with MFC or MEC have been developed to enhance electricity production and wastewater treatment or to drive H_2 or CH_4 generation [10-15]. MRC and MREC are more effective than traditional MFC and MEC on energy capture [10, 12, 16, 17]. Especially the MREC has been proved as an attractive alternative to

the MEC for H₂ generation without external power supply [16]. In this context, MREC could be an alternative technology to MEC for cost-effective and efficient H₂O₂ production, which has never been reported before. Therefore, it is meaningful to explore the feasibility of H₂O₂ production in the MREC.

The performance of MREC is affected significantly by the number of cell pairs and salinity gradients between high concentration salt water (HC, eg., seawater) and low concentration salt water (LC, eg., fresh water), which are well studied [11, 18]. However, another key challenge of the MREC is that a large amount of seawater and fresh water are required. To make the MREC an economically attractive technology for chemical synthesis (e.g., H₂O₂), the feasibility of recycling the salt and fresh water for minimizing the water consumption needs to be demonstrated. Besides, control of cathode potential for effective H₂O₂ formation could be another challenge, as the MREC is operated without external power supply or potentiostat. Cathode potential has been identified as the key parameter for H₂O₂ production in MEC [8, 19]. In different systems, the H₂O₂ concentration and optimal cathode potential might differ greatly. Sim et al. investigated the H₂O₂ concentration at cathode potential of -0.4 V, -0.6 V, -0.8 V with O₂ provision (aqueous and gaseous O₂) in MEC, and the maximum H₂O₂ concentration was achieved at cathode potential of -0.4 V [8]. However, in another MEC study, the maximum H₂O₂ concentration only was 39.8 ± 10.4 mg L⁻¹ at the optimal cathode potential of -1.4 V (vs Ag/AgCl) [7]. Thus, the interaction between H₂O₂ production and cathode potential in the MREC needs to be investigated.

In this study, we developed and investigated the MREC as an alternative way to produce H₂O₂. The influential operating parameters such as air flow rate, initial catholyte pH, synthetic salt and fresh water flow rate and catholyte concentration were investigated. The key limiting factors to the cathode potential were also identified. Furthermore, the recycling

of salt and fresh water and its impact on H_2O_2 production were demonstrated. To the best of our knowledge, this is the first time that the salinity-gradient energy harvested by the MREC was used to drive the H_2O_2 synthesis. This work not only demonstrates a novel method for H_2O_2 synthesis, but also offers a potential platform technology for sustainable wastewater treatment.

2. Material and methods

2.1. Reactor setup and operation.

The schematic diagram of the MREC reactor is shown in Fig. 1. As previously described [16]. The MREC consisted of anode chamber and cathode chamber, which were separated by a RED stack. The RED stack comprised five cell pairs, each consisting of a cation exchange membrane (CEM) (CMI 7000, membrane international, NJ) and an anion exchange membrane (AEM) (AMI 7001, membrane international, NJ), with alternately high concentration NaCl solution (35 g L^{-1}) as synthetic salt water and low concentration NaCl solution (0.35 g L^{-1}) as synthetic fresh water flowing in between. Additionally, at the end of the stack next to the cathode, one additional AEM was used as a shielding membrane to close the last cell. The anode was a carbon fiber brush (5.0 cm diameter, 5.0 cm length, Mill-Rose, USA), which was heated to 450°C for 30 min in a muffle furnace before use [20]. The cathode was a graphite plate ($3 \text{ cm} \times 3 \text{ cm}$). Ag/AgCl electrode ($+0.197 \text{ V}$ vs SHE) as reference electrode was placed $\sim 0.5 \text{ cm}$ apart from the cathode electrode to measure the cathode potential, all the cathode potential reported here were vs. Ag/AgCl reference electrode. The carbon fiber brush anode was first enriched with biofilm in a MFC using domestic wastewater collected from primary clarifier (Lyngby Wastewater Treatment Plant, Copenhagen, Denmark) together with acetate sodium (20 mM) as substrate [9], and then transferred into the anode chamber of MREC. The working volume of the anode chamber was

100 mL ($5\text{ cm} \times 5\text{ cm} \times 4\text{ cm}$). In order to avoid substrate limitation on the system performance, the anode chamber was continuously fed with the domestic wastewater amended with acetate sodium ($\sim 1.6\text{ g-COD L}^{-1}$ in total) at 50 mL d^{-1} . The cathode chamber ($5\text{ cm} \times 5\text{ cm} \times 2\text{ cm}$) was filled with 40 mL NaCl solution and operated in batch mode. Prior to a new batch run, the cathode chamber was rinsed three times using NaCl solution. Air was bubbled into the catholyte continuously using a peristaltic pump at different flow rate as stated later on. Unless otherwise stated, the initial catholyte pH was 7, NaCl solution was 35 g L^{-1} , the air flow rate was fixed at 12 mL min^{-1} , HC and LC solution flow rate was fixed at 0.5 mL min^{-1} . Four control reactors were also setup under the following conditions: Control 1, both HC and LC solutions were $0.35\text{ g L}^{-1}\text{ NaCl}$ solution; Control 2, open circuit; Control 3, no air flow in cathode chamber; Control 4, no microorganisms on the anode. All experiments were carried out in duplicate at room temperature ($22 \pm 2\text{ }^{\circ}\text{C}$).

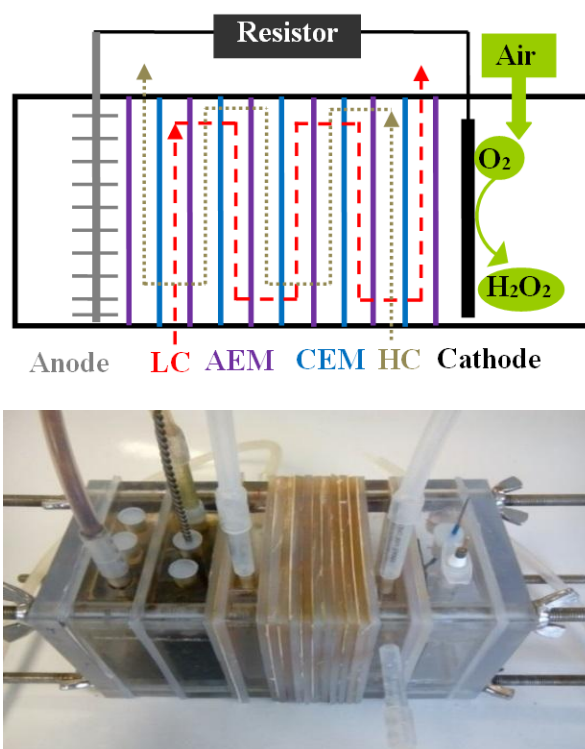


Fig. 1. Schematic of MREC (CEM: cation exchange membrane, AEM: anion exchange membrane, HC: high concentration solution, LC: low concentration solution).

2.2. Electrochemical and chemical analysis and calculations.

The pH was measured using a pH meter (PHM 210 pH meter, Radiometer). The H₂O₂ concentration was measured by UV-vis spectrophotometry (Spectronic 20D+, Thermo Scientific), using potassium titanium (IV) oxalate as colored indicator [21]. Chemical oxygen demand (COD) was measured according to the Standard Method [22]. The voltage across on one 10 Ω external resistor (load) was monitored with 30 min intervals using a digital multimeter (model 2700, Keithley Instruments, Inc., Cleveland, OH, USA) [23], and the power output was calculated ($P = U^2/R$).

Coulombic efficiency (CE, %) was calculated based on total consumption of the COD as previously described [10]. Cathodic H₂O₂ efficiency (R_{cat}) was defined as the cumulative H₂O₂ production actually at the cathode compared to the theoretical amount that could have been produced from the current (based on consuming 2 mol e⁻ to produce 1 mole H₂O₂) [6].

Electrical energy input was defined as the total electrical energy consumption expressed as charge divided by the cumulative H₂O₂ production in the MREC system. The electrical energy consumption was measured by a sparometer (Type NZR230, S.L. Energitekinik, Denmark). The calculations of Coulombic efficiency (CE), Cathodic efficiency (R_{cat}) and electrical energy input per kg H₂O₂ production are shown in the Supplementary materials.

3. Results and discussion

3.1. The feasibility of H₂O₂ production in MREC.

The evolution of H₂O₂ concentration in the MREC is shown in Fig.2. The H₂O₂ concentration increased gradually with time and reached around 778 ± 11 mg L⁻¹ at 72 h (Fig. 2A). No further increase of H₂O₂ was observed with longer operation time, which indicated that the accumulated H₂O₂ reached steady state, the same trend also have been reported in MFCs and MECs [8, 24]. This behavior could be due to that the H₂O₂ generation, reduction of H₂O₂ on

the cathode and self-decomposition of H_2O_2 might occur simultaneity in the H_2O_2 electrogeneration process [25, 26]. In addition, the pH increase with the reaction time, which could also promote the H_2O_2 self-decomposition in cathode [24]. The H_2O_2 production was also investigated under different control conditions. No significant H_2O_2 production was observed in the control reactors during the same operation time. The H_2O_2 concentration in the reactors without salinity gradient in the RED (HC and LC were in same salt concentration, Control 1), with open circuit (Control 2), without air flow in the catholyte (Control 3) and without microorganisms on the anode (Control 4) was 83 ± 1.5 , 0, 20.1 ± 1.9 and 32.9 ± 2.8 mg L^{-1} , respectively (Fig. 2A).

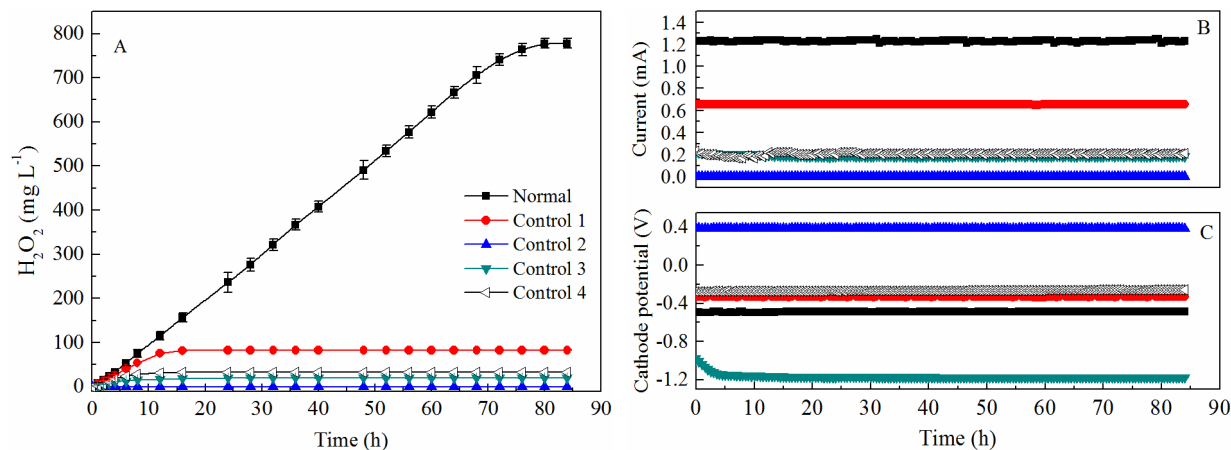


Fig. 2. The performance of MREC under normal and different control conditions (Normal: air flow rate of 12 mL min^{-1} , catholyte pH of 7, 0.5 mL min^{-1} HC and LC solution flow in RED; Control 1: both HC and LC solution are 0.35 g L^{-1} NaCl solution; Control 2: Open circuit; Control 3: No air flow in cathode chamber; Control 4: No microorganisms on the anode).

Along with H_2O_2 production, the current and cathode potential were investigated. As shown in Fig. 2B, the current was very stable and around 1.23 mA while the cathode potential was -0.48 V during H_2O_2 production (in Normal Condition). Comparatively, the current observed in all the control reactors were much lower. Unlike current, the cathode potentials were varied in different control reactors. The cathode potential in the reactors with same HC

1 and LC flow in the RED (Control 1), with open circuit (Control 2), without air flow in the
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3 catholyte (Control 3) and without microorganisms on the anode (Control 4) was about -0.33,
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5 +0.39, -1.17 and -0.27 V, respectively (Fig. 2C). These results demonstrated the RED stack,
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7 dissolved oxygen in the catholyte and anodic biofilm are the key factors for H₂O₂ generation,
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9 which can affect the cathode potential, current and H₂O₂ concentration in the MREC.
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13 H₂O₂ synthesis and its reduction to water were simultaneously occurring in the cathode.
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15 Thus, the maximum H₂O₂ concentration that can be reached could be varied in different
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17 bioelectrochemical systems, which are important for the further use of the products in
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19 commercial applications, such as integration with Fenton reaction for wastewater treatment.
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23 The performance of the MREC on H₂O₂ production was compared to that of the previously
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25 reported METs, as summarized in Table 1. It is obvious that the production concentration of
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27 H₂O₂ was much higher than that of MFC systems, which was due to the optimal electrical
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29 potential generated by the RED stack. The H₂O₂ concentration produced by the MREC was
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31 comparable to that of the MEC. The H₂O₂ concentration observed in this study was even
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33 higher than that achieved in a MFC-MEC-coupled system or a MEC with 0.5 V external
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35 voltage supply [4, 27]. In a recent MEC study, a maximum H₂O₂ concentration of 1447 mg L⁻¹
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37 was achieved [8]. Though this value is higher than the one achieved in this study, the
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39 advantage of the MREC is obvious as the MEC needs an external power source to supply
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41 much higher voltage ranging from 1.24 to 1.69 V [8], which is not needed for the MREC.
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Table 1. Performance of H₂O₂ synthesis using different microbial electrochemical technologies

METs	Cathode	External voltage (V)	Cathode potential (V)	Current density (A m ⁻²)	H ₂ O ₂ concentration (mg L ⁻¹)	Production rate (μmol h ⁻¹)	Reference
MFC	Graphite	-	-	18.41 ^d	196.50	35.8	[4]
MFC	Graphite	-	-	25.40 ^d	78.20	-	[27]
MFC	Graphite	-	-0.25	-	78.85	13.5	[5]
MEC	Graphite	0.50	-	5.30±0.70	~1300	1596±163.8	[6]
MEC	Graphite with carbon black	0.60	-	-	39.80±10.40	1.35	[7]
MEC	Graphite	a	-1.20~-1.70	7.70±0.60	1447	29.03	[8]
MEC	Graphite	b	-	2.40	439	-	[9]
MEC	Graphite	c	-	2.79	700	-	[28]
MEC	Graphite	0.50	-0.85	-	711.20	13.07	[27]
MREC	Graphite	-	-0.48	1.37±0.09	778±11	13.53±0.59	This study

a: control the cathode potential using a potentiostat.

b: one MFC power the MEC

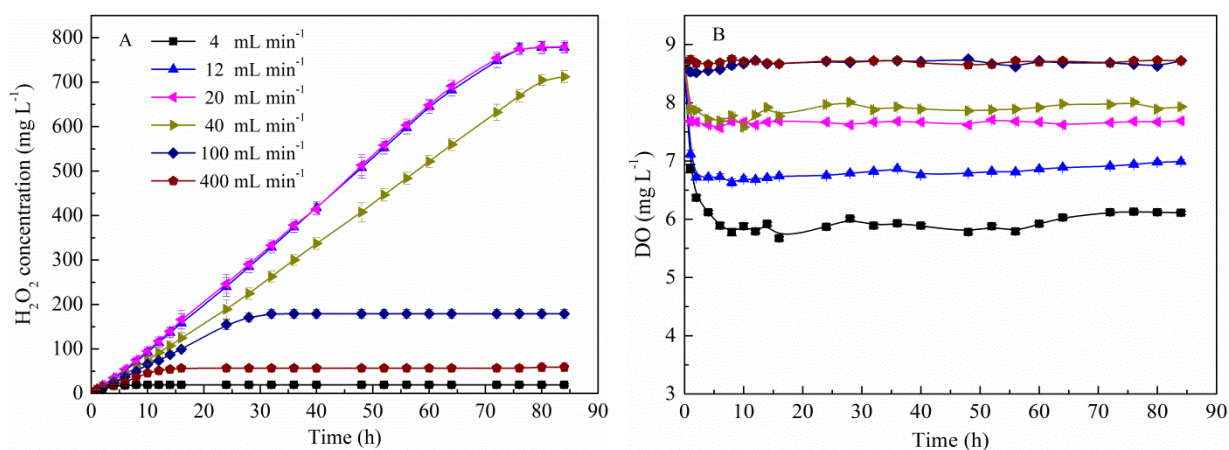
c: control the current by a potentiostat.

d: current density (A m⁻³)

3.2. Effect of air flow rate.

Oxygen is the electron acceptor at the cathode of the MREC, so its availability could be crucial to H₂O₂ production. Thus, the effect of air flow rate on H₂O₂ production, cathode potential, current and dissolved oxygen (DO) were studied at HC and LC flow rate of 0.5 mL min⁻¹, initial catholyte pH of 7. The results are shown in Fig. 3. The concentration of H₂O₂ increased dramatically with the increasing of air flow rate in a certain range, in particular when the air flow rate increasing from 4 to 12 mL min⁻¹ (Fig. 3A). The corresponding H₂O₂ concentration increased from 19 ± 2.5 to 778 ± 11 mg L⁻¹. When the air flow rate was increasing from 12 to 20 mL min⁻¹, no further increase in the H₂O₂ concentration was observed. The H₂O₂ concentration was kept at 779 ± 14 mg L⁻¹. However, further increase the air flow rate above 20 mL min⁻¹, the H₂O₂ concentration decreased significantly. For example, when the air flow rate increased from 20 to 400 mL min⁻¹, the H₂O₂ concentration decreased from 779 ± 14 to 59 ± 10 mg L⁻¹. The behavior was similar with that observed in the traditional H₂O₂ electrogeneration process [29]. In addition, it also has been reported that the air flow rate could affect the concentration of H₂O₂ in dual-chamber MFC reactor [24]. Fig.

3B shows the trend of DO with the increasing of air flow rate. The DO value increased also with increasing of air flow rate in a certain range. For example, the DO value increased significantly from 5.9 ± 0.2 to 8.6 ± 0.2 mg L⁻¹ with the increase of air flow rate from 4 to 100 mL min⁻¹. The DO value maintained at 8.6 ± 0.2 mg L⁻¹ when the air flow rate was further increased to 400 mL min⁻¹. The results indicate that from 12 to 20 mL min⁻¹ the oxygen saturation in the cathode was not reached, at the air flow rate over 20 mL min⁻¹. The observed decrease of H₂O₂ production was due to oxygen saturation that enhanced the further degradation of H₂O₂. It is generally considered that a high O₂ flow rate is beneficial for H₂O₂ generation in electrosynthesis system, since high air flow rate could enhance the DO in the solution and promote the mass transfer rate, which is favorable for the H₂O₂ accumulation [8, 29]. However, excessive air supply might lead to the stoichiometric imbalance of H₂O₂ production process (eq.1) [24]. At the same time, the higher air flow rate could also disturb the mass transfer between catholyte and electrode and result in a low catalytic efficiency for H₂O₂ generation [21,30]. These results further indicate the importance of air flow rate to the H₂O₂ generation in the MREC.



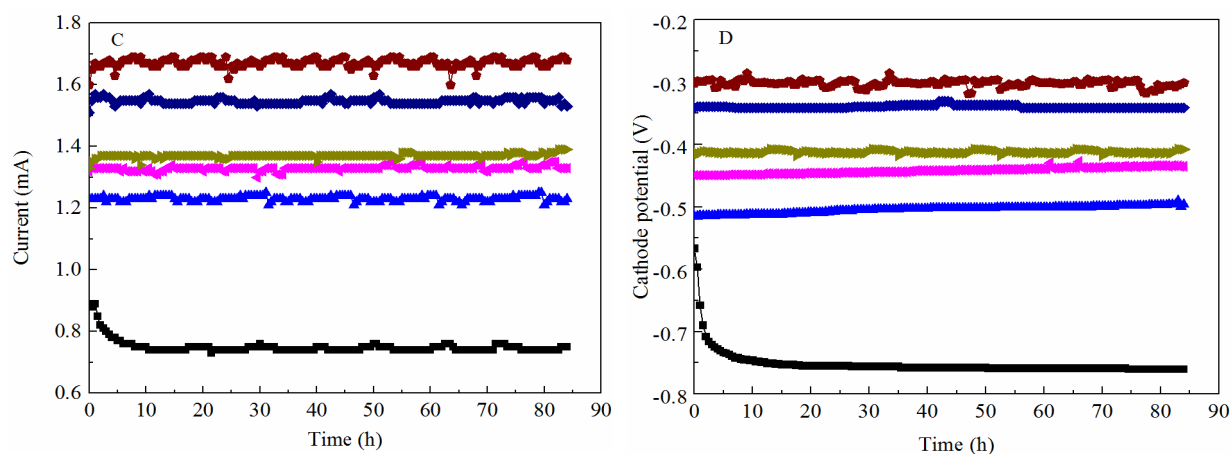


Fig. 3. The effect of air flow rate on the concentration of H_2O_2 (A), DO (B), Current (C) and Cathode potential (D).

It has been previously proved that the cathode potential and current are two key factors for H_2O_2 production in METs [8,28]. External power sources or potentiostat can be used to control the cathode potential and current at the suitable value for improving H_2O_2 concentration and production rate. In the MREC, the RED stack was placed between the cathode and anode to replace the external power source. In order to further explain the correlations related to the air flow rate, the cathode potential and current output were recorded. Fig. 3C and Fig. 3D show the trend of current and cathode potential in a certain range of air flow rate. Interestingly, when the air flow rate was increased, the corresponding cathode potential became less negative and the current increased significantly. A maximal current of 1.68 ± 0.03 mA and cathode potential of -0.310 ± 0.05 mV were achieved with the air flow rate of 400 mL min^{-1} . However, the maximal H_2O_2 concentration was obtained at the air flow rate of 12 to 20 mL min^{-1} , the corresponding cathode potential were ranging from -0.505 ± 0.005 to -0.442 ± 0.006 V. The optimal cathode potential for H_2O_2 generation was different in different METs (see Table 1). In generally, the two-electron reaction (eq.1), four-electron reaction (eq.2) and the H_2O_2 decomposition reaction (eq.3 and 4) occur simultaneously on the surface of cathode [27, 31]. The results indicate that the two-electron reaction (eq. 1) producing H_2O_2 was the dominant reaction in the MREC when the air flow rate was 12 to 20 mL min^{-1} , because the H_2O_2 reduction (eq. 3 and 4) was slower than the H_2O_2 formation. Vice-versa, at higher air flow, the lower H_2O_2 formation indicates that eq. 2 might dominate. Therefore, the choice of a suitable air flow rate is important for the practical application in the future.



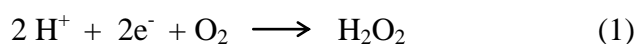
3.3. Effect of initial catholyte pH.

The generation of H_2O_2 was also carried out at different initial pH values, during which the changes of pH values were monitored. The effect of initial catholyte pH in the MREC was investigated at HC and LC flow rate of 0.5 mL min^{-1} , air flow rate of 12 mL min^{-1} . As shown in Fig. 4A, when the initial pH values were 2, 3, 5, 7 and 10, the H_2O_2 concentrations reached to 786 ± 18 , 783 ± 16 , 779 ± 15 , 778 ± 11 and $777 \pm 14 \text{ mg L}^{-1}$, respectively. The results indicate that the initial catholyte pH has no significant effect on the accumulated H_2O_2 concentration, which was in agreement with traditional H_2O_2 electrogeneration processes [31]. There was a slight decrease of H_2O_2 accumulation with the increasing pH value between 2 and 7 in the first four hours, but no significant difference on the H_2O_2 production rate and concentration were observed between pH 7 and pH 10 during the same period. Since H_2O_2 was generated on the cathode surface by the reduction of oxygen with H^+ , a low pH would be beneficial to increase H_2O_2 production rate. That could be the explanation to the relatively higher H_2O_2 production rate at low pH in the first few hours.

The variation trend of the catholyte pH is shown in Fig. 4B. When the initial pH values were 3, 5 and 7, the pH rapidly becomes alkaline after 1 h, while it took 3 hours when the initial pH was 2. The final catholyte pH increase to ~ 12.5 regardless of the initial pH. This observation is similar with previous MREC studies focusing on electrical energy production [10]. When the cathode pH turned to alkaline condition, there were no significant difference on the H_2O_2 production rate and concentration. The results explained why the H_2O_2

production rate turned to be similar after a few hours. The results also demonstrated that the H_2O_2 production in the cathode of the MREC was possible both in acidic and alkaline conditions, which was consistent with the observation in the abiotic electrochemical processes for H_2O_2 production (eq.1, eq.5 and eq.6) [2]. Thus, pH adjustment in the cathode could be omitted, which may reduce the costs in the practical application. The above results indicate the unique advantages of the MREC for H_2O_2 synthesis in a wide range of pH values.

Acid solutions:



Neutral and Alkaline solutions:

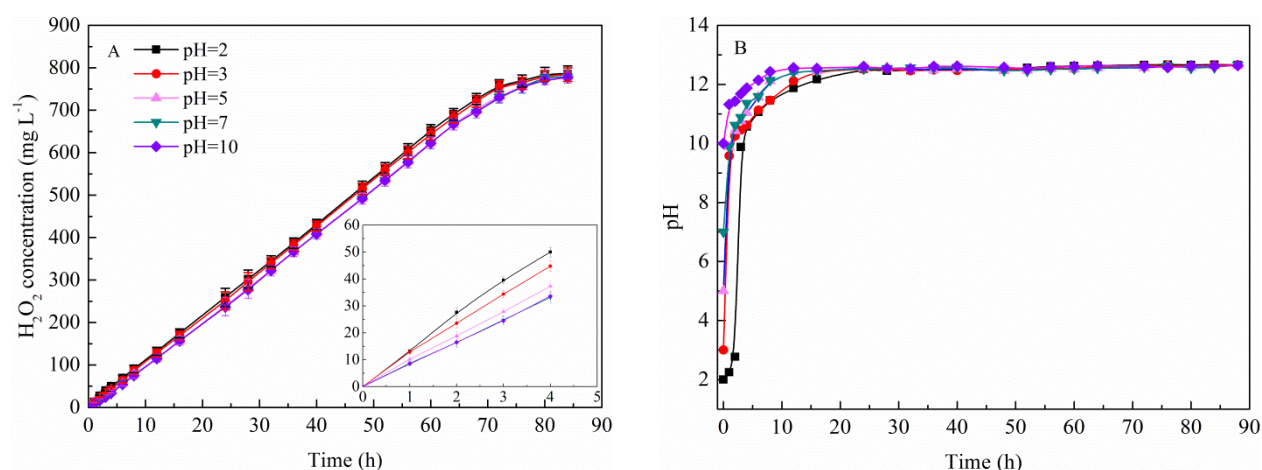
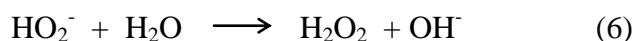
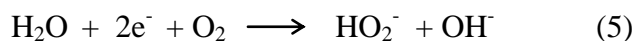


Fig. 4. The effect of initial pH on the H_2O_2 production in the MREC.

3.4. Effect of HC and LC solution flow rate.

The performance of H_2O_2 production was investigated with the flow rates of the HC and LC solutions ranging from 0.2 to 6 mL min⁻¹. As shown in Fig. 5A, an increase in flow rate from 0.2 to 0.5 mL min⁻¹ resulted in a significant increase in the H_2O_2 concentration and production rate. When the flow rate increased from 0.5 to 2 mL min⁻¹, the H_2O_2 concentration and

production rate were maintain at maximum values of $778 \pm 11 \text{ mg L}^{-1}$ and $11.5 \pm 0.5 \text{ mg L}^{-1} \text{ h}^{-1}$ (Fig. 5A). Further increase the flow rate to 6 mL min^{-1} , there was no significant changes of H_2O_2 concentration. However, there was a small decrease in the H_2O_2 production rate. The electrical output can be improved through increasing the solution flow rate within a certain range in RED, and then a relatively high current is beneficial to the H_2O_2 production. However, higher flow rates also lead to high ohmic losses, as there was no enough time to complete the ion transportation through membranes which maintained the influent LC and HC salinity throughout the RED [10, 33]. Thus, a small decrease of the current and the production rate were observed at the flow rate of 6 mL min^{-1} . Consistent with the current, the cathode potential was varied in the range of -0.5 to -0.4 V at different solution flow rates (Fig. 5B). With respect to the maximum H_2O_2 concentration and production rate, the cathode potential was maintained at $0.45 \pm 0.04 \text{ V}$ at the solution flow rate of 0.5 mL min^{-1} .

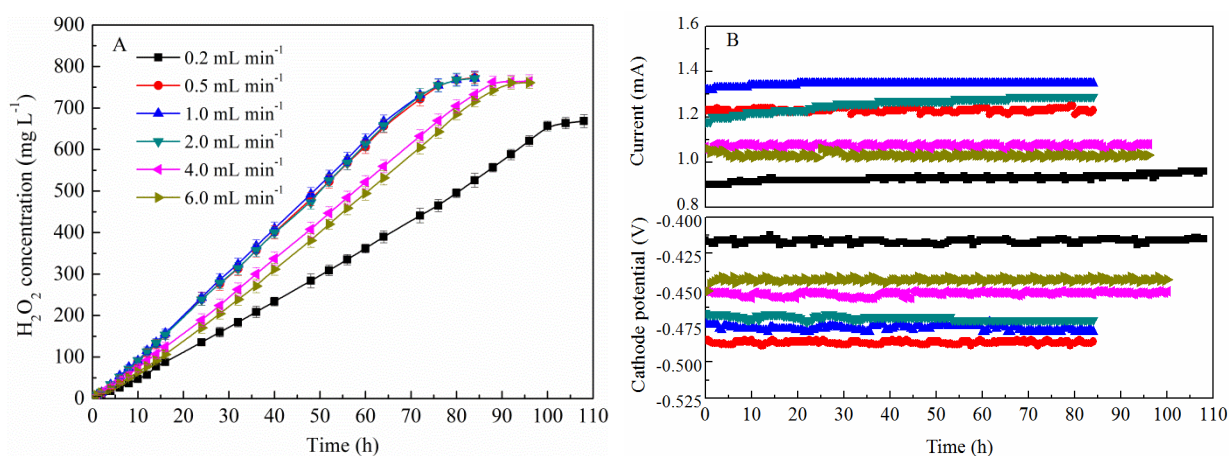


Fig. 5. The effect of HC and LC flow rate on the H_2O_2 production.

The flow rate not only impacted the H_2O_2 production, but also affected the energy required to pump the HC and LC solutions through the RED stack. The pumping energy is an important part of the costs for RED operation, and thus, a low flow rate is preferred for practical applications [34]. In order to obtain maximum H_2O_2 concentration with minimum

energy costs for MREC operation, the optimum flow rate was considered to be 0.5 mL min^{-1} based on the above results (Fig. 5A).

3.5. Performance with recycling HC and LC solution.

A commercial MREC installation should aim at high concentration of H_2O_2 production with low water consumption in a certain range. In order to further reduce the energy cost and water consumption, the recyclability of the HC and LC solution were investigated at 0.5 mL min^{-1} flow rate. As shown in Fig. 6A, the concentration of LC increased with the increasing of recycle time, while the concentration of HC showed opposite trend. Thus, the salinity ratios became smaller and smaller, *eg.*, after 13 cycles, the salinity ratio between HC and LC solution decreased from 100 to 2.5. The H_2O_2 concentration was maintained at $778 \pm 11 \text{ mg L}^{-1}$ during the first 9 cycles. When the HC and LC were recycled after 9 cycles, the H_2O_2 concentration and current started to decrease (Fig. 6B), while the cathode potential began to increase. A possible explanation could be that the decreasing of salinity ratio decreased electrochemical junction potential in the RED stack [12], and then resulting in the change of cathode potential. The behavior is similar with the H_2 production in MREC.

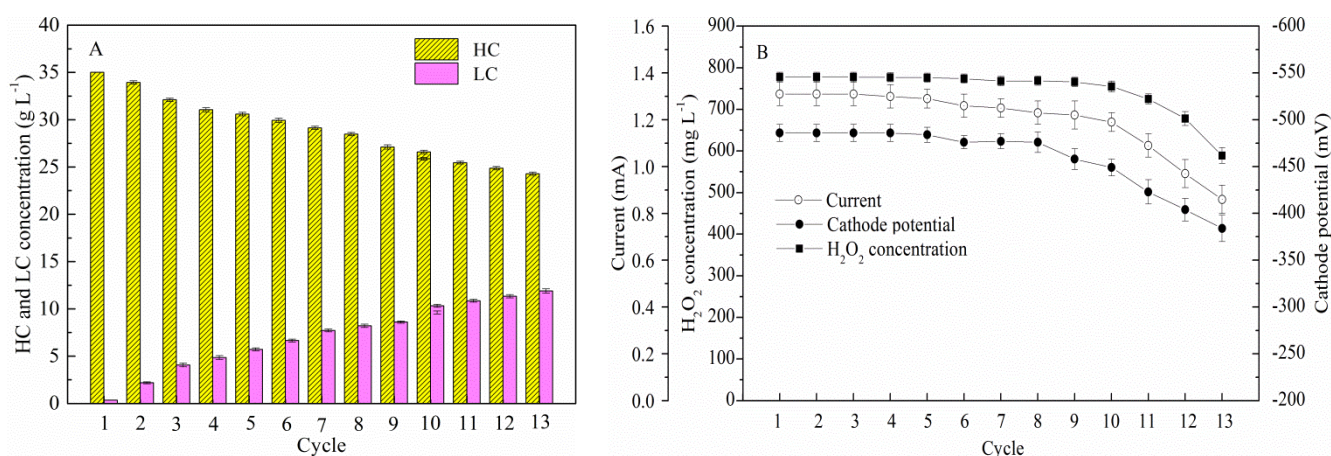


Fig. 6. The effect of HC and LC concentration on H_2O_2 generation.

During each cycle, the anolyte pH was maintained at neutral (data is not shown) under continuous flow mode, which exclude the inhibition of anodic biofilm caused by anolyte pH [10, 35]. The COD removal efficiency was above 85% in all these cycles (data is not shown). These results for the first time demonstrated the feasibility of simultaneously recycling the HC and LC solutions in MREC, especially for H₂O₂ production, which offer insight on scaling up the technology with less water consumption. Furthermore, the results also indicate the applicability of MREC with broad salinity ratios between HC and LC solution without deteriorating the system performance on H₂O₂ production.

3.6. Effect of catholyte concentration.

The power density of RED can be increased upon increasing the concentration of electrolyte [36]. To investigate the effect of catholyte concentration on H₂O₂ generation, the experiments were carried out with initial cathode pH of 7, air flow rate of 12 mL min⁻¹ and HC and LC flow rate of 0.5 mL min⁻¹. As shown in Fig. 7, the catholyte concentration had significant impact on the H₂O₂ production. The H₂O₂ concentration increased from 45 ± 10 to 778 ± 11 mg L⁻¹ with the increasing of NaCl concentration from 0 to 21 g L⁻¹, when further increase the concentration to 35 g L⁻¹, no increase on H₂O₂ concentration were observed. This result also suggests that the H₂O₂ could be produced by using deionized water as catholyte, although the final H₂O₂ concentration is low. The catholyte concentration also influenced the current, *eg.*, the current increased significantly from 0.76 ± 0.03 to 1.29 ± 0.08 mA with the increasing of catholyte concentration from 0 to 21 g L⁻¹. Further increase the concentration to 35 g L⁻¹, the current value had no appreciable change. The observation could be due to that the catholyte conductivity and ionic strength increased with the increasing of catholyte concentration and thereby improving the current and H₂O₂ concentration. However, the improvement on the current turned to be steady-state when the catholyte concentration exceeded a certain range.

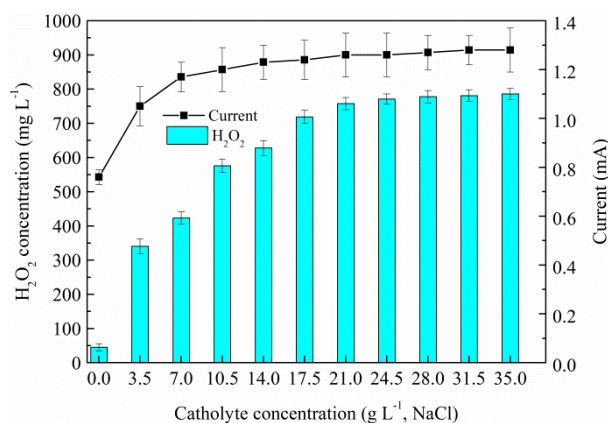


Fig. 7. The effect of catholyte concentration on H₂O₂ generation.

3.7. Energy consumption and efficiency

In the light of H₂O₂ concentration and the energy consumption, the HC and LC flow rate of 0.5 mL min⁻¹ and air flow rate of 12 mL min⁻¹ are the optimal choice for the H₂O₂ production in this MREC system, the energy input (0.45 ± 0.03 kWh kg⁻¹ H₂O₂) was significantly lower than that of MEC systems for H₂O₂ production, which require about 0.66~0.93 kWh kg⁻¹ H₂O₂ [6, 27]. In addition, the H₂O₂ production cost is lower than the price of commercial bulk H₂O₂ which is about 1.5 \$ per kg H₂O₂ [32]. The coulombic efficiency was only $14.96 \pm 0.86\%$, while the COD removal reached $86.25 \pm 0.75\%$ in the anode fed with real wastewater.

Power output of the MREC was stable at $15.13 \pm 0.25 \mu\text{W}$ (see Fig.S1, Supplementary data).

The low CE could be due to the oxidation of organic matters by the nonexoelectrogenic microorganisms from wastewater. The cathodic efficiency was $53.26 \pm 0.68\%$, which is better than previous reports of 42% [32]. Moreover, the synthesized water through oxygen reduction reaction only was 0.0067 ± 0.0005 mL, it is not significant. Despite the cumulative H₂O₂ production in the MREC system still is low for large-scale industrial application, the rather low energy cost for H₂O₂ production still makes the technology very promising. Table 2 summarizes energy consumption under eight different conditions.

Table 2. The COD removal, R_{cat} , CE and energy input under different operation conditions.

Air flow rate (mL min ⁻¹)	HC and LC flow rate (mL min ⁻¹)	Anolyte COD removal (%)	R_{cat} (%)	Energy input (kWh kg ⁻¹ H ₂ O ₂)	CE (%)
12	0.5	86.25 ± 0.75	53.26 ± 0.68	0.45 ± 0.03	14.96 ± 0.86
20	0.5	85.64 ± 0.65	49.65 ± 0.56	0.54 ± 0.03	15.49 ± 0.58
40	0.5	86.47 ± 0.53	42.58 ± 0.42	0.62 ± 0.02	15.53 ± 0.67
12	0.2	86.35 ± 0.36	41.98 ± 0.44	0.49 ± 0.04	11.56 ± 0.87
12	1.0	86.53 ± 0.86	47.49 ± 0.31	0.48 ± 0.04	14.97 ± 0.49
12	2.0	85.64 ± 0.76	49.32 ± 0.29	0.48 ± 0.03	14.18 ± 0.76
12	4.0	84.54 ± 0.72	51.25 ± 0.45	0.51 ± 0.03	12.44 ± 0.97
12	6.0	84.63 ± 0.46	51.45 ± 0.66	0.51 ± 0.03	12.35 ± 0.85

3.8. Significance and perspectives

The present work for the first time demonstrated the applicability of the MERC for H₂O₂ production. Compared to other microbial electrochemical systems such as MFC and MEC, MREC has its own merits. Firstly, the H₂O₂ production was greatly improved by employing the RED stacks between the anode and cathode, compared to the MFC. Secondly, no external power source is needed as the potential created by the RED stacks reactor can accelerate the electron transfer for cathode reduction, compared to the MEC. Thirdly, the energy consumption was only 0.45 ± 0.03 kWh kg⁻¹ H₂O₂ under optimal operation condition, which indicated that the MREC is an energy-efficient system for synthesis of H₂O₂.

Though promising, more efforts should be made to accelerate the industrial application. First of all, the H₂O₂ concentration still needs to be improved to the level which meets the industrial implications. The volume of H₂O₂ generated in present study was insignificant (less than 0.1 ml) compared to the catholyte volume (40 ml) (Table S1). To obtain pure or high H₂O₂ concentration and simultaneous to save the energy for product separation, a moist open-to air cathode could be used [37, 38]. Secondly, this is a proof-of-concept study, while a more cost-effective and efficient reactor configuration needs to be developed for the field application. For instance, single porous ceramic membrane that can more easily serve the purpose of driving the electro-osmosis and remove the need for a whole bunch of synthetic

membranes could be interesting for future studies on system optimization. Thirdly, to further consolidate the in-situ utilization of the produced H_2O_2 , it would be interesting to integrate the MREC with various environmental bioremediation processes such as advance oxidation processes for water treatment. In addition, it could be also interesting to use high salt feedstock in the anodic chamber in future studies as there were some electrochemically active bacteria that can grow naturally in sea water, urine and other salty environments [39, 40]. All these together will make MREC an attractive platform technology for the electrosynthesis of H_2O_2 and potentially utilization of salinity-gradient energy.

4. Conclusions

In this study, the MREC system was for the first time developed for microbial electrosynthesis of H_2O_2 from oxygen reduction. High H_2O_2 concentration of $778 \pm 11 \text{ mg L}^{-1}$ was obtained without utilizing any external power source. The cathode potential as the key factor for H_2O_2 electrosynthesis was affected by the air flow rate. In addition, the H_2O_2 production was affected by catholyte concentration. Moreover, it showed a good performance for the electrochemical reduction of O_2 to H_2O_2 in a wide range of pH (2–10). Furthermore, no deterioration in H_2O_2 production was observed by recycling the salt and fresh water in the first 9 cycles. The energy costs for the H_2O_2 synthesis using MREC was as low as $0.45 \pm 0.03 \text{ kWh kg}^{-1} \text{ H}_2\text{O}_2$. All these features indicate that MREC is an attractive method for the electrosynthesis of H_2O_2 .

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Figure 1

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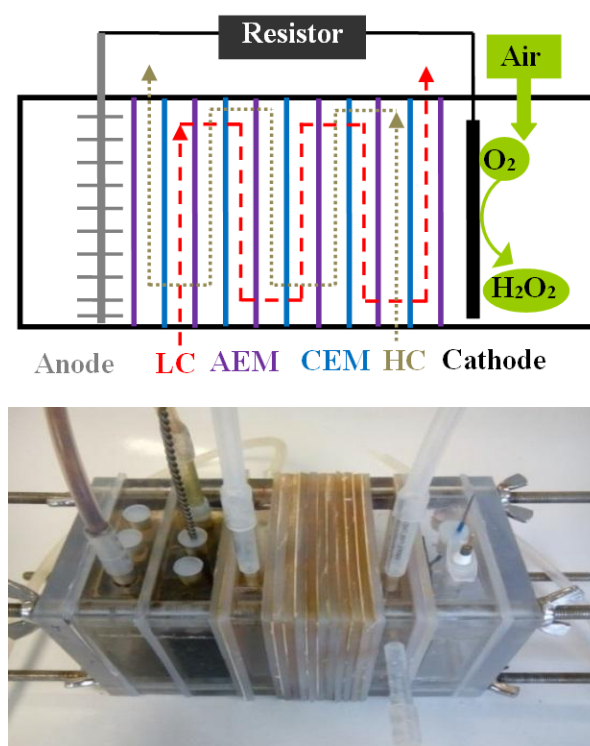


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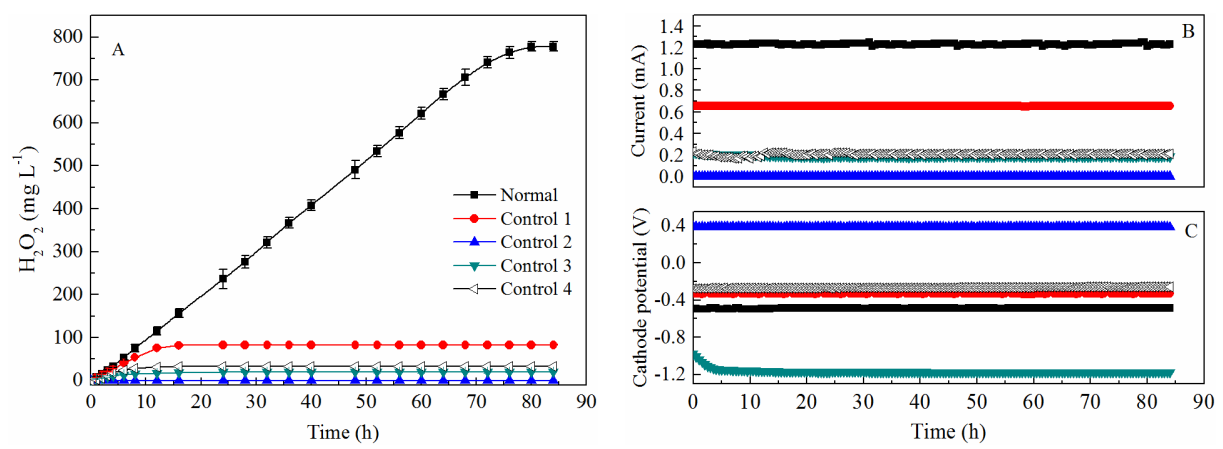


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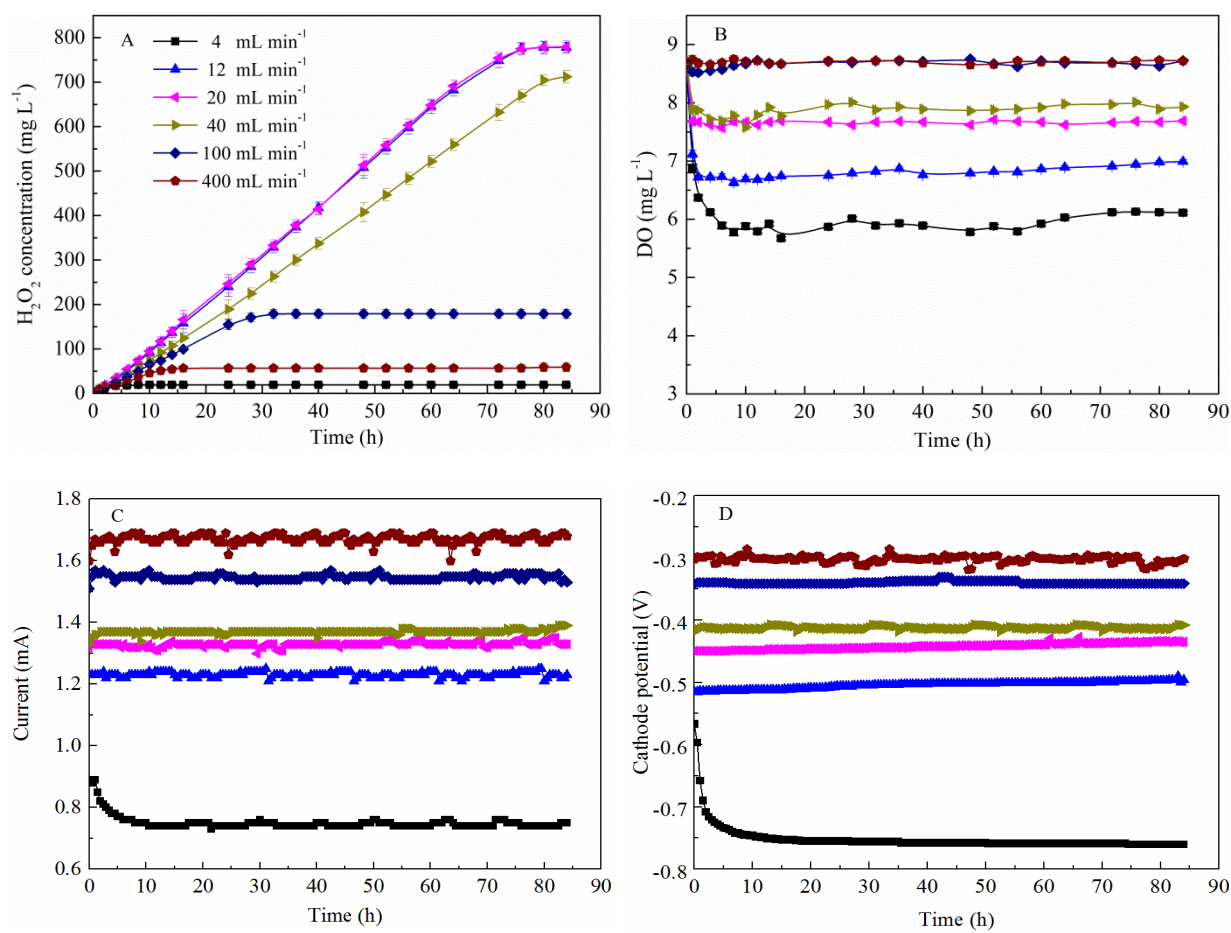


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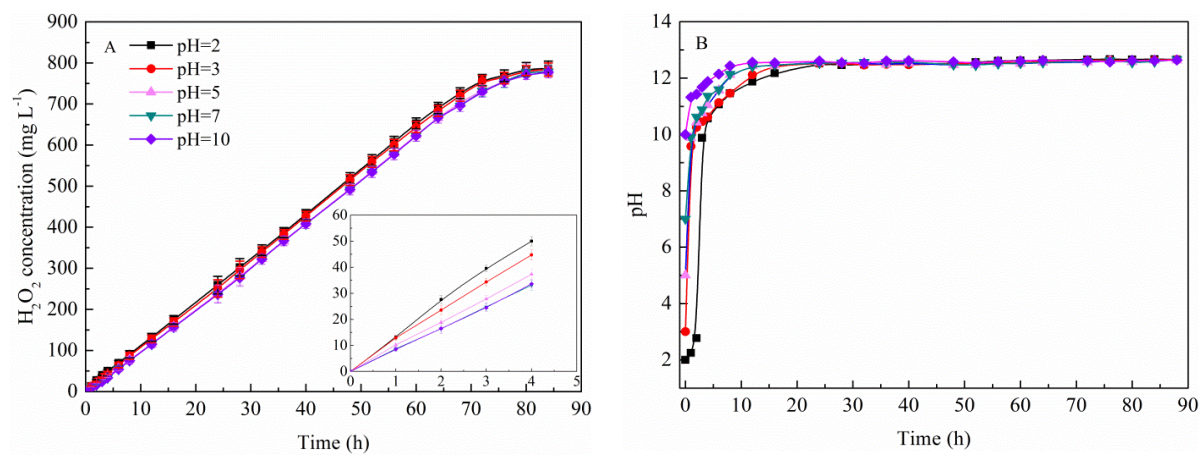


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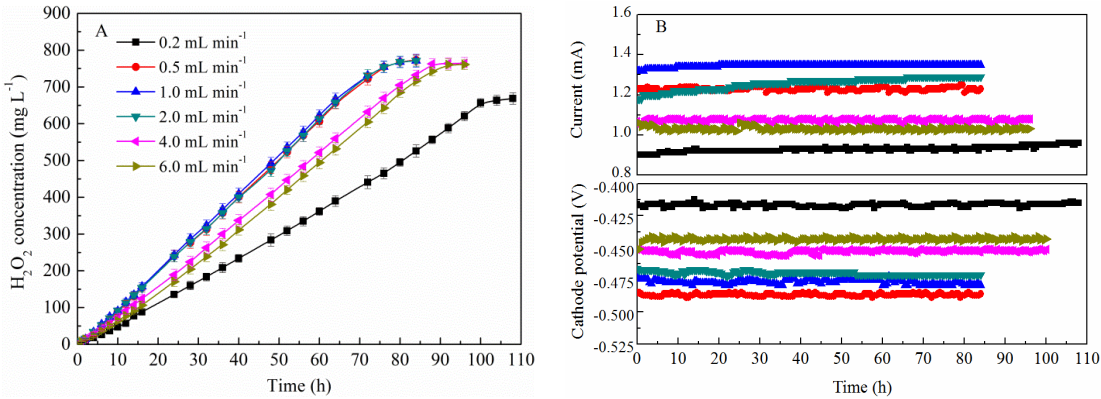


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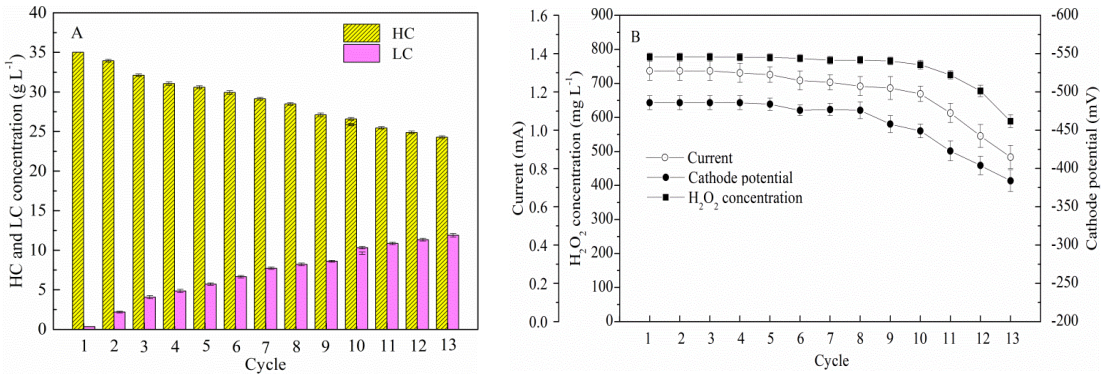


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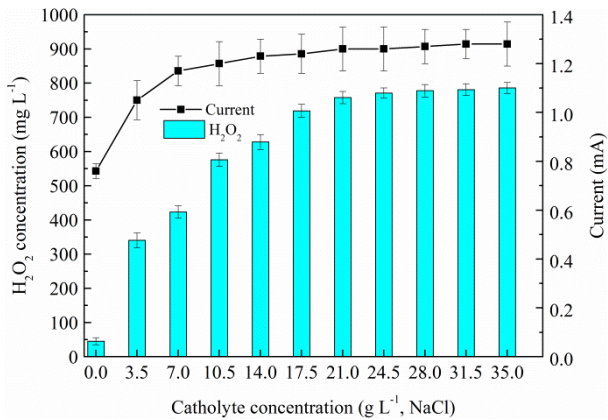


Fig. 7.

Figure and table captions

Fig. 1. Schematic of MREC (CEM: cation exchange membrane, AEM: anion exchange membrane, HC: high concentration solution, LC: low concentration solution).

Fig. 2. The performance of MREC under normal and different control conditions (Normal: air flow rate of 12 mL min⁻¹, catholyte pH of 7, 0.5 mL min⁻¹ HC and LC solution flow in RED; Control 1: both HC and LC solution are 0.35 g L⁻¹ NaCl solution; Control 2: Open circuit; Control 3: No air flow in cathode chamber; Control 4: No microorganisms on the anode).

Fig. 3. The effect of air flow rate on the concentration of H₂O₂ (A), DO (B), Current (C) and Cathode potential (D).

Fig. 4. The effect of initial pH on the H₂O₂ production in the MREC.

Fig. 5. The effect of HC and LC flow rate on the H₂O₂ production.

Fig. 6. The effect of HC and LC concentration on H₂O₂ generation.

Fig. 7. The effect of catholyte concentration on H₂O₂ generation.

Table 1. Performance of H₂O₂ synthesis using different microbial electrochemical technologies

Table 2. The COD removal, R_{cat} , CE and energy input under different operation conditions.

Supplementary Materials

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